PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
H01L 31/0384, 51/20, 51/30, 33/00

A1

(11) International Publication Number: WO 99/25028

(43) International Publication Date: 20 May 1999 (20.05.99)

(21) International Application Number: PCT/EP98/07328

(22) International Filing Date: 11 November 1998 (11.11.98)

(30) Priority Data:
97203499.5 11 November 1997 (11.11.97) EP

(71) Applicant (*for all designated States except US*): UNIVERSITEIT VAN UTRECHT [NL/NL]; Heidelberglaan 8, NL-3584 CS Utrecht (NL).

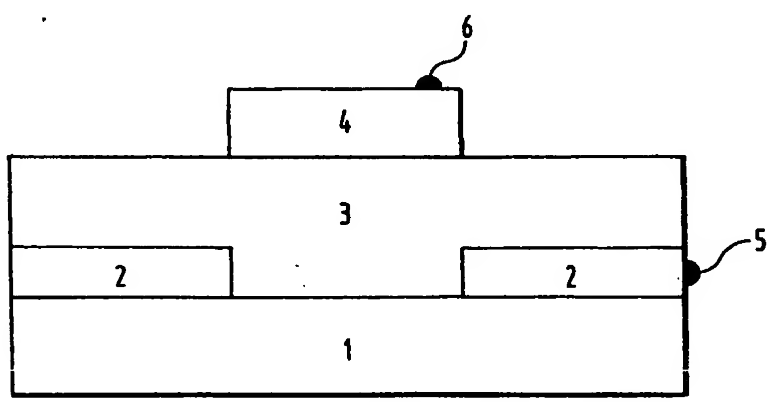
(72) Inventors; and
(75) Inventors/Applicants (*for US only*): SCHROPP, Rudolf, Emmanuel, Isidore [NL/NL]; Rosariumlaan 15, NL-3972 GE Driebergen (NL). SALAFSKY, Joshua, Samuel [NL/NL]; Nieuwe Gracht 36M, NL-3542 LS Utrecht (NL).

(74) Agent: LAND, Addick, Adrianus, Gosling; Arnold & Siedsma, Sweelinckplein 1, NL-2517 GK The Hague (NL).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: POLYMER-NANOCRYSTAL PHOTO DEVICE AND METHOD FOR MAKING THE SAME



(57) Abstract

The present invention relates to a photo device comprising a layer of nanometer sized particles and a conducting polymer in solid state, wherein the nanometer sized particles are chosen from the group of TiO_2, ZnO, CdSe, CdS, ZrO_2 and SnO_2; and wherein the conducting polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

POLYMER-NANOCRYSTAL PHOTO DEVICE AND METHOD FOR MAKING THE SAME

Especially for reducing costs for photovoltaic cells, research is done all around the world for finding a solid state composition of creating an interpenetrating solid-state conducting material in a nanoporous network. Such device could also be used for LED (Light Emitting Diodes), photo sensors, optical switches and even optical networks.

The present invention relates to a photo device comprising a layer of nanometer sized particles and a conducting polymer in solid state, wherein the nanometer sized particles are chosen from the group of TiO_2, ZnO, CdSe, CdS, ZrO_2 and SnO_2, and wherein the conducting polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

Prior methods have been published on the insertion of a polymer electrolyte into a preformed nanocrystalline TiO_2 (titanium dioxide) network (F. Cao et al., Proceedings of Nanostructured Materials in Electrochemistry, held: Reno, NV, USA, 21-26 May 1995). These methods have, however, the disadvantage of being based on an ionic conductor. The device performance is therefore limited. The ionic conductor is not suited for electronic devices.

Another prior method using conducting polymers (PPV and derivatives) replaces the inorganic nanocrystalline network with C_{60} and derivatives which act as electron-acceptors (G. Yu et al., Science 270 (1995) 1789). However, in this method, the electron transport is restricted. Further, C_{60} is not a material which is produced abundantly, and is expensive; it is also much less stable than inorganic materials.

Another prior method using a conjugated polymer, poly(2-methoxy, 5-(2'-ethyl)-hexyloxy-p-phenylenevinylene; MEH-PPV), incorporates nanoparticles of CdS or CdSe (N.C. Greenham et al., Physical Review B. Condensed Matter, 54 (1996) 17628, N.C. Greenham et al., Synthetic Metals 84 (1997) 545-546), but the cadmium-containing compounds have a disadvantage in that they are carcinogenic and also not abundantly available.

Another publication (S.A. Carter et al., Applied Physics Letters 71 (1997) 1145) discloses the use of TiO_2 nano-particles blended with electroluminescent organic material in light emitting diodes. As an example, MEH-PPV was tested as organic material. The mixtures were spin cast onto an Ito coated glass, whereafter the solvent was evaporated off. The device lacks photovoltaic properties.

The present invention has for its object to offer a solution to the problem of creating an interpenetrating solid-state conducting material in a nanoporous network, for the purpose of creating stable, all-solid state photovoltaic cells. The instability problems associated with liquid based electrolytes in nanoporous networks (B. O'Regan et al., Nature, 353 (1991) p737) are to be avoided.

A further object of the present invention is to offer a photovoltaic cell, which offers the stability, electron transporting properties, the abundant availability, the low costs, and the no-toxicity of TiO_2 in an interconnected network in combination with the hole-transporting, light-absorbing, stable properties of PPV (poly-paraphenylenevinylene).

A further aspect of the present invention is the ease of manufacturing, namely in a single thermal treatment of the inorganic and organic materials together. The thermal treatment is elegantly simple, and provides for converting the polymer precursor to its final, conducting form as well, as for producing electrical contact between the inorganic nanometer sized

particles to make continuous electron-carrying pathways to the end terminal of the photovoltaic cell, the object of the present invention.

None of the above prior art methods use a mixture of a polymer precursor in solution and inorganic nanometer sized particles in a colloidal solution to produce an interpenetrating composite layer in a single step of thermal treatment.

A preferred embodiment of the method according to the present invention uses a conducting polymer precursor (poly(p-xylene-alpha-tetrahydrothiophene-bromide; p-PPV) and a nanocrystalline material, TiO_2.

Further advantages, features and details of the present invention are elucidated in the following description, which refers to the enclosed figures, in which:

fig. 1 is a diagrammatic cross section view of a device according to the present invention; and

fig. 2 is a graph of current voltage characteristic of the device of fig. 1.

A schematic cross section of the cell is shown in fig. 1. The polymer p-PPV was made by chemical synthesis (J.J.M. Halls et al., Nature 376 (1995) 498), the TiO_2 nanocrystals were obtained from Degussa AG Corporation, Germany. An approximately 0.7% methanolic solution of the p-PPV was combined with a colloid of TiO_2 (the colloid had been made according to Nazeeruddin et al., J. Am. Chem. Soc. 115 (1993) 6382), to give a mixture of approximately 1:1 p-PPV and TiO_2 by weight. This mixture was spin-coated on a glass substrate 1 with a transparent conducting coating 2, in this example SnO_2:F, to give a thin film 3. The film was heated to 320°C for ten hours in vacuum and an aluminum contact 4 was evaporated in such a way that there was no overlap with the transparent conducting coating on the glass on top of the film to complete the cell.

Current-voltage (IV) curves of the cells in the dark and in substantially white light were measured at

terminal 5 and 6 (fig. 1) and a plot of this data is shown in fig. 2 which demonstrates that the cells produce electric power under illumination.

At least the thermal treatment step of the present invention is novel and inventive over the prior art. This step provides for both conversion of the p-PPV to its conducting form, PPV and for producing electrical contact between the TiO_2 particles to produce electron-carrying paths through the film.

The method according to the present invention allows the use of precursor polymer and thus the complex process of first synthesizing MEH-PPV before blending with nanoparticles. Moreover, the method, by starting from a mixture of a colloid of TiO_2 and a solution of p-PPV, also provides a solution to the very poor penetration of conducting polymers with high molecular mass into a preformed porous nanocrystalline semiconductor.

The present method is first in making operational photovoltaic cells of a conducting polymer, such as PPV, and a sintered electrically interconnected network of nanocrystalline particles, such as TiO_2.

PPV has been shown to be a good hole-conducting material and TiO_2 an excellent electron transporter, so their combination together, prepared in a single thermal treatment step, provides a significant advantage.

The present invention is not limited to the embodiment described; the rights applied for are defined in the annexed set of claims; the scope of protection includes other polymers and nanocrystals, as well as other temperatures.

CLAIMS

1. A photo device, comprising a layer of nanometer sized particles and a conducting polymer in solid state.

2. A photo device according to claim 1, wherein the nanometer sized particles are chosen from the group of TiO_2, ZnO, CdSe, CdS, ZrO_2, SnO_2, Al_2O_3, SiO_2.

3. A photo device according to claim 1 or 2, wherein the conducting polymer is a conjugated polymer with the functionalities of light absorption and charge transporting properties.

4. A photo device according to claim 1, 2 or 3, in which the conjugated polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

5. A photo device according to claim 1, 2, 3 or 4, wherein the layer is a thin film of a photovoltaic cell.

6. A method for producing a photo device, according to claim 1, wherein the layer is made by mixing the nanometer sized particles in a colloid with precursor PPV.

7. A method according to claim 6, wherein the precursor PPV is poly(p-xylene-alpha-tetrahydrothiophene bromide).

8. A method according to claim 6, wherein the mixture of TiO_2 and PPV is between 10:90 and 70:30 by weight.

9. A method according to claim 6, for producing a photo device, according to claim 1, wherein the layer is heated to a predetermined temperature during a predetermined time.

10. A method according to claim 9, wherein the heating takes place in an inert gas, at substantially underpressure, or vacuum.

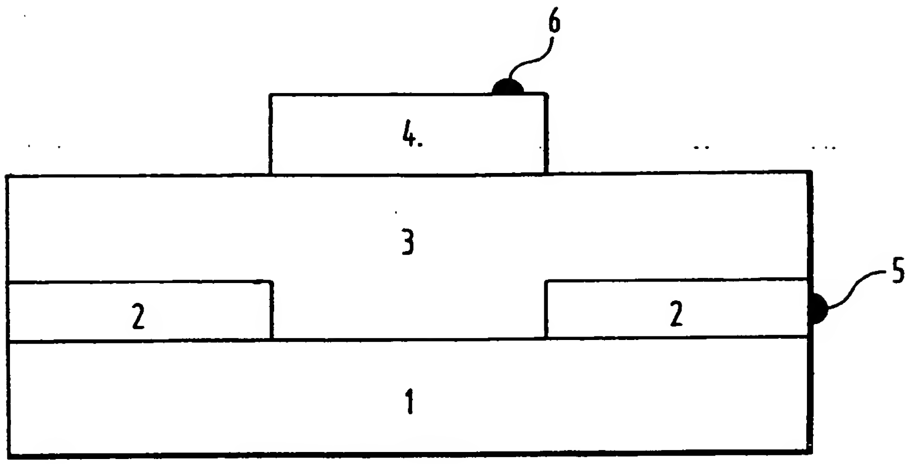

6
4.
3
5
2
2
1

FIG. 1

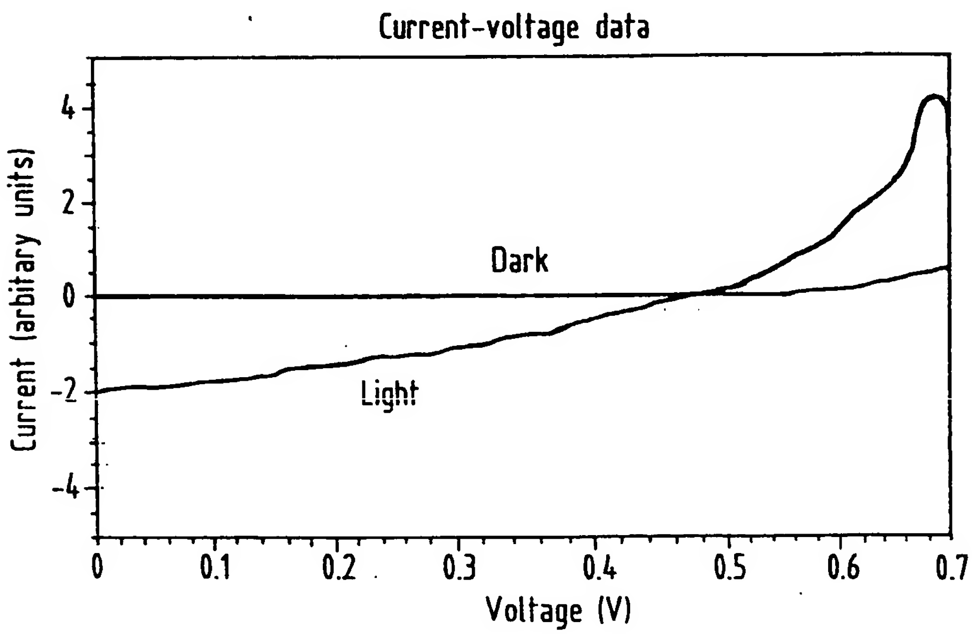

Current-voltage data
Current (arbitrary units)
4
2
0
-2
-4
Dark
Light
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Voltage (V)

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/07328

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01L31/0384 H01L51/20 H01L51/30 H01L33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	N.C. GREENHAM ET AL.: "Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity" PHYSICAL REVIEW, B. CONDENSED MATTER., vol. 54, no. 24, 15 December 1996, pages 17628-17637, XP002060964 NEW YORK US cited in the application see page 17628 - page 17630	1-5

-/--

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 March 1999	12/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Visentin, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/07328

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	N.C. GREENHAM ET AL.: "Charge separation and transport in conjugated polymer/cadmium selenide nanocrystal composites studied by photoluminescence quenching and photoconductivity" SYNTHETIC METALS, vol. 84, no. 1-3, 1 January 1997, pages 545-546, XP002060965 AMSTERDAM, NL cited in the application see the whole document	1-4
X	S.A. CARTER ET AL.: "Enhanced luminance in polymer composite light emitting devices" APPLIED PHYSICS LETTERS., vol. 71, no. 9, 1 September 1997, pages 1145-1147, XP000720223 NEW YORK US cited in the application see page 1145	1-4
A	KUCZKOWSKI A: "THE PROSPECTS FOR POLYESTER POLYMER-CDS POWER COMPOSITES IN PHOTOELECTRONIC DEVICE APPLICATIONS" JOURNAL OF PHYSICS D. APPLIED PHYSICS, vol. 22, no. 11, 14 November 1989, pages 1731-1735, XP000072966 BRISTOL, GB see the whole document	1-5,9,10
A	HALLS J J M ET AL: "EFFICIENT PHOTODIODES FROM INTERPENETRATING POLYMER NETWORKS" NATURE, vol. 376, 10 August 1995, pages 498-500, XP000578123 cited in the application see the whole document	1,3-5,9,10

1